NASA

Technical Memorandum **82001**

Investigation Of Electrical Noise In Selenium - Immersed Thermistor Bolometers

John L. Tarpley and Pedro D. Sarmiento

AUGUST 1980

National Aeronautics and
Space Administration

Goddard Space Flight Center
Greenbelt, Maryland 20771

TM 82001

INVESTIGATION OF ELECTRICAL NOISE IN SELENIUM-IMMERSED THERMISTOR BOLOMETERS

John L. Tarpley and Pedro D. Sarmiento
Materials Control and Applications Branch

August 1980

GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland 20771

CONTENTS

ILLUSTRATIONS

INVESTIGATION OF ELECTRICAL NOISE IN SELENIUM-IMMERSED THERMISTOR BOLOMETERS

John L. Tarpley and Pedro D. Sarmiento

ABSTRACT

The selenium-immersed, thermistor-bolometer, IR detector has a history marked by failure due to spurious and escalating electrical noise outburst as a function of time at elevated temperatures. These failures were observed during routine ground-based testing in a space-simulated environment. Spectrographic analysis of failed bolometers revealed selenium-pure zones in the insulating selenium-arsenic (Se-As) glass film which surrounds the active sintered Mn, Ni, Co oxide flake. The selenium-pure film was identified as a potentially serious failure mechanism. Therefore, significant changes were instituted in the manufacturing techniques and, along with more stringent process controls, these changes effectively eliminated the selenium-pure film and successfully produced 22 study bolometers.

Independent bolometer testing of electrical stability at two different test laboratories gave conflicting test results on unsealed units. Barnes laboratory tests revealed no anomalous noise fluctuations or excursions on 22 units whereas Ithaco laboratory tests showed a very rapid noise buildup on 11 units tested by them. The reason for the conflict was not determined. However, bolometers that were deliberately sealed as required for space flight use and then tested up to 50°C for 2000 hours continuously performed well within electrical noise specifications at Ithaco.

INVESTIGATION OF ELECTRICAL NOISE IN SELENIUM-IMMERSED THERMISTOR BOLOMETERS

INTRODUCTION

The bolometer study reported here was prompted by the failures of two epoxy-sealed bolometers during ground-based operational tests of the infrared (IR) horizon scanners from the HCMM and SAGE Spacecraft. Both failures began as a gradual increase in electrical noise level which later escalated into a major problem after 498 hours of test for one unit and 639 hours for the other. A study of the problem at that time did not reveal the cause of the electrical noise,[1] but did suggest the need for further investigation. Bolometer failures had been reported as early as 1970 and electrical noise breakdown presumably constituted the primary failure mode.[2] Lockheed[2] stressed better quality control in manufacturing as a starting point toward reducing failures. Lockheed also established a direct correlation between bolometer noise breakdown and device exposure to temperatures up to 60°C. The subject investigation included a study of the bolometer manufacturing techniques and quality control procedures with particular attention given to the bolometer elements which might exhibit radical or critical changes at elevated temperatures.

DESCRIPTION

Thermistor bolometer devices are IR detectors uniquely suited for spacecraft horizon sensor applications, attributed mainly to their volume efficiency, light weight, and low power dissipation. Each bolometer is custom-built for each specific application. The heart of the bolometer is pin-head size heat sensing thermistor flake. In 1978, a survey showed that two manufacturers were marketing selenium (Se) immersed bolometers; namely, Barnes Engineering of Stamford, CT and Servo Corporation of Hicksville, NY. This report will confine itself to the investigation of the Barnes Bolometers.

An overall view of the metal-case, plug-in type bolometer is shown in Figure 1. Flat germanium (Ge) lenses, as shown, were used in these experimental devices to reduce cost and were considered satisfactory for test purposes. However, hemispherical Ge lenses are required for flight units to accurately focus IR radiation onto the flake.

Just seven critical parts, described below, make up the internal construction of the Barnes bolometer. These are represented in the line drawing of Figure 2 and are detailed in Figure 3. A brief description of each part follows.

(1) The flake is an IR radiation-sensitive thermistor, consisting of a 10μm thin composite layer of oxides of Manganese (Mn), Nickel (Ni), and Cobalt (Co). The exact proportion of the three oxides is proprietary. A thermistor is a thermally-sensitive resistor with a negative temperature coefficient of electrical resistance whose rate of change in this application is approximately 4%/°C.

(2-3-4) One-mil-diameter platinum (Pt) lead wires are bonded to each end of the flake after it has had a layer of gold (Au) applied by vapor deposition. Before lead wire attachment, the Pt wire ends are dressed with a Au-filled organic slurry, then this Au coated wire is carefully placed on the Au coated flake surface and subsequently fired in a furnace. The pin-head size flake is more easily handled with the leads attached and is then given a vacuum deposit of a 2μm thick film of selenium arsenic (Se-As), vapor deposited on the side opposite the lead attachment. Flakes are then stored until required to complete the assembly of a bolometer.

(5) A Ge lens focuses incoming IR radiation onto the body of the thermistor flake and also serves as its heatsink. Lenses vary in radii from 3.5 mm to 8.3 mm.

(6) The flat surface of the lens receives a thin, but opaque, layer of vapor deposited aluminum (VDA), applied through a mask to provide a distinct pattern used to stop stray radiation from striking the thermistor flake.

(7) An electrical insulating Se-As film is vapor deposited on the VDA and on the exposed Ge surface at the center of the lens, left open in the VDA pattern. The thermistor flake is imbedded into the heat softened Se-As layer at the center of the lens. A layer of Se-As, about 2μm thick, is then vapor deposited on the exposed flat surface of the immersed flake.

(8) The unit is placed in a gold-plated copper-case which is evacuated and is epoxy-sealed, Figure 1.

MANUFACTURING TECHNIQUE AND QUALITY CONTROL

The manufacturing and quality control procedures used by Barnes Engineering were thoroughly examined. It was determined that these procedures were not as tightly controlled as necessary for space flight hardware. It was, therefore, stipulated in the work statement that the following steps be incorporated in the manufacturing process:

1. Platinum leads be masked during Se-As evaporation.
2. In-process visual inspection be made at 100 times magnification instead of 30 times.
3. SEM inspection be made of all immersed bolometer flakes.
4. Only one flake-immersion heat-up cycle be permitted in each bolometer construction process.
5. Firing schedule of flakes, called annealing by Barnes, be held to a time period of 2 hours ± 15 mins. rather than a random firing schedule.

In addition, a basic change was made in the process of evaporating the Se-As mixture. The source of the Se-As composite mixture contained Wt% proportions of either 92 Se to 8 As or 88 Se to 12 As. The final evaporated film should have been approximately these percentages. Instead, the film that was deposited during an initial evaporation phase was much richer in Se than desired, showing in fact no detectable amount of As. The old procedure allowed for complete exposure of the bolometer thermistor elements to the vaporized stream during the entire deposit period from the initial heatup of the Se-As source material, to the final cutoff temperature of 380°C, a period of about three minutes. This procedure was questioned because of the difference in evaporation temperatures of Se and As at 10^{-6} torr, vacuum pressure at which the depositions are made. The RCA Honig/Kramer vapor pressure (VP) tables show that the 10^{-6} torr VP occurs at 107°C for Se and at 179°C for As, a difference of 72°C. This means that at 10^{-6} torr Se vaporizes at a temperature 72°C lower than that of As, allowing for a near 100% Se-rich film layer to be deposited first. The presence of the near pure Se layer was subsequently confirmed at the GSFC, the details of which are discussed later in this paper.

To prevent Se-pure film depositions, Barnes was requested to install a manually controlled stainless steel shutter mechanism in the deposition path whose function was to block all film deposits from the bolometer elements for about three minutes, or until the Se-As mixture reached its final evaporation temperature of 380°C. At that time, the shutter was opened to allow deposition of the composite film mixture. The improvement in film deposit control was confirmed experimentally. Diagrammatic sketches in Figure 4 show how Se-pure film layers were interposed within the old bolometer construction and were absent from the new construction.

Using the new techniques, a number of experimental film specimens, (i.e., devices which excluded the thermistor flake) were constructed and used for IR transmission and auger electron

spectroscopy (AES) studies. Twenty four (24) complete bolometers were constructed and used to investigate sensitivity to elevated temperatures.[4] These contained less expensive Ge disc, rather than the standard hemispherical Ge lens to support the thermistor flake. All devices were left unsealed to permit periodic visual inspections following each temperature test.

LABORATORY ANALYSIS

AES was used to study the composition of the vapor deposited films. As mentioned earlier, the study of the films from the old evaporation procedure revealed a layer near 100% rich in Se at the flake surface for both the 8 wt% As and 12 wt% As samples. This is in contrast to the uniformly distributed, 10μm thick films of Se-As mixture deposited by the new evaporation procedure. These two contrasting Auger spectra are explicitly revealed in Figures 5 through 7. Figure 5 shows characteristic Se peaks without the presence of As at the thermistor flake. The heights of the peaks are not totally indicative of the quantity of an element present, but are more a function of the specimen's position or distance relative to the Auger detector, the Auger sensitivity to the element in question, and the constitution of the sample itself. The flake material is represented in the plot by the Mn, Ni, and Co peaks. Carbon (C), Sulphur (S), and oxygen (O) peaks are found in most all Auger plots and are there as trace amounts of impurities. Frequently, the O is part of an oxide layer. Argon (Ar) is the ionized gas used to sputter off the surface. Silver (Ag) is not an element of the bolometer. It was painted on the surface as a conductive stripe around the edges of the flake to prevent electron charging at the Se-As surface during SEM analysis.

Figure 6 represents a sample of a uniformly mixed film layer of Se and As at the Ge substrate. Both Figures 6 and 7, were of specimen samples made by the new evaporation technique. The same Auger spectrum was obtained for both the 8 wt% and 12 wt% As. The Auger procedure normally used to chemically analyze film layers is by a depth profile analysis. This procedure identifies the

elements and simultaneously provides a continuous plot of each element in the film from the top surface to the bottom surface. However, this film definition technique was not possible in this analysis due to the highly insulating Se-As film ($\S 10^{12}$ ohms) which caused distortions and erratic movement of the Auger electron beam at the film surface. Thus, the film was identified in discrete steps represented by Figures 5 through 7.

IR transmission spectra were obtained of film specimens from both the old and the new film deposition techniques. Spectra were recorded on a perkin-Elmer 621 Spectrophotometer prior to heat treatment and immediately after heat treatment in air for one hour at 134°C. Such a temperature exposure closely simulated the standard heat cycle that bolometer components are normally subjected to during a flake immersion. The IR spectrum from the old evaporation technique, Figure 8, showed a scattering effect in the films, as indicated by the shift in the pre and post heat curves. The sine wave patterns denote interference fringes that are directly correlated to film thickness; approximately 10μm for these films.

The net effect of such scattering was a loss in transmission, as much as 25% of peak to peak values at wavelengths in the 10.5 to 11.5μm region. There was no scattering for those films from the new evaporation process, as shown in Figure 9. In addition, no substantive differences in IR transmission were found between samples with 8 wt% and 12 wt% of As.

A more extensive study of the effects of heat on the properties of Se has been performed by M. K. El-Mously[3] who found that amorphous Se transforms to the crystalline state when heated above 90°C and that crystalline Se is more electrically conductive than amorphous Se. He also found that by simply adding a small percentage of As (5 At%) to the Se, crystallization of the amorphous Se was inhibited. Therefore, it is imperative to have some As in the Se glass film to prevent Se crystal transformation, especially at elevated temperatures.

In the subject study, the proportion of Se and As in the starting pellet granules, and that of the resultant evaporated film, was investigated by means of Energy Dispersive Analysis of X-rays (EDAX). Samples from both 8 wt% and 12 wt% As, as initially proportioned, were analyzed and the semi-quantitative results are presented in Table 1. The EDAX yields results in atomic percent (At%). Due to the close proximity of Se (Z = 34) and As (Z = 33) in the periodic table, the wt% and At% of the compositions are practically the same, as shown below.

	Wt%	At%	Wt%	At%
Se	92	91.6	88	87.4
As	8	8.4	12	12.6

The initial Se-As mixtures were proportioned as shown in Column II in Table 1. These mixtures were melted, quenched, then broken into small pellets. The EDAX analysis of individual pellets is shown in Column III where it is seen that mixtures of the same composition yielded pellets of different composition, e.g. samples 2942 and 2945. Also, the glass films deposited on the bolometer were not the same when referenced from one to the other or to the source. However, no appreciable differences in electrical performance were noted from these various film compositions. It is vital, as noted earlier, that some As be in the film. The results indicated that the amount of As, whether 8% or 12%, was not critical. The data in Table 1 show that each time the Se-As mixture is heated, the percent of As increases, indicating the tendency of Se to evaporate more easily. This fact was used as the basis for the installation of the shutter in the manufacturing process.

TEMPERATURE TESTS

Each of the 24 bolometers was initially subjected to a series of electrical tests to assure that they met acceptable performance levels and to establish a data base for all subsequent measurements.

The electrical noise output level was the most critical parameter monitored. Other electrical parameters measured as well were:

- Detector time constant
- Signal voltage with 0.6 peak voltage bias
- Peak voltage
- Noise voltage in the 5-100 Hz bandwidth with 0.6 peak bias voltage and with no bias voltage
- Bandwidth
- Electrical resistance between the two flakes and from each flake to the Ge flat, with 0 6 peak voltage applied in dual polarity.

The 24 new bolometers consisted of 12 each of 8 wt% As and 12 wt% As in the original Se-As pellet mixture.* The sampling scheme of the 12-unit lots for thermal exposure at Barnes was:

- 5 units with 0.6 peak bias voltage applied
- 5 units without bias and
- 2 control units left in ambient room conditions.

Twenty (20) units were then exposed sequentially to thermal tests of the following conditions:

- 1 week (168 hrs.) at 50°C
- 1 week (168 hrs.) at 60°C and
- 3 weeks (504 hrs.) at 70°C.

Following each level of exposure, all units, including the 4 controls, were electrically tested. The criterion for failure was one microvolt (μV) maximum of noise voltage. No failures occurred.

*Two of the 12 wt% As units were accidentally burned out when overvoltage stressed during bench testing.

The results from the thermal exposures, presented as average values for each lot, are displayed in Figures 10 and 11. The maximum noise level for any one device never exceeded 0.72 μV and overall results were very typical of a standard bolometer burn-in. The climb in overall noise level after 60°C exposure is attributed to the fact that the initial test set malfunctioned and was temporarily removed for repairs. The 60°C measurement was, therefore, made on a backup test set resulting in a slight perturbation in the noise response. Nevertheless all measurement were well within specification.

It is noted that Barnes Engineering rates this type of bolometer up to a maximum temperature of 40°C. The 20 unsealed units in this study survived temperatures up to 70°C for 840 hours without failure which represents a new performance level for this device. (Servo Corporation rates their devices up to 60°C).

Subsequent to thermal testing at Barnes, Ithaco, Inc., was contracted to perform a 1000-hour life test on 11 randomly selected noise free devices from both the 8 wt% and 12 wt% As lots.[5] Ithaco had in their possession a GFE custom-built bolometer life test assembly designed by them and used previously to test sealed, flight-qualified bolometers. They had not, however, previously tested unsealed, experimental type bolometers such as used in this study. Based on the successful thermal tests at Barnes, it was expected that the life test would be routine, but it was not. Each of the 11 units in the Ithaco test developed excessive electrical noise within 36 hours of the initial test exposure. Six of these noisy devices were returned to Barnes for retesting and all six were found to be noisy at Barnes also. Laboratory investigations into this behavior were conducted jointly by the GSFC, Barnes[4] and Ithaco,[5] but the combined efforts did not explain the conflicting results. It should be noted that such bolometer behavior occurred only at Ithaco on unsealed bolometers which had already been thermally tested at Barnes for 840 hours at temperatures up to 70°C without a problem.

At this point, Barnes was contracted to seal two of the remaining noise-free devices in metal cans such as shown in Figure 1. These two units were life tested at Ithaco in an identical test configuration as the unsealed units. Both survived an extended life test at 50°C while biased at 0.6 peak voltage without showing any evidence of noise build-up. One was tested for 2000 hours and the other, available later, for 1000 hours.

A totally separate bolometer, not part of the 24 experimental test lot, had its seal broken for test purposes and then was placed in storage at Ithaco for one year. It was subsequently tested at Ithaco together with the two sealed units. This unsealed device also broke down with excessively high electrical noise outputs, thus confirming the susceptibility to electrical noise generation in unsealed devices at Ithaco.

Meanwhile, four more of the remaining unsealed, noise-free devices from the original 24-unit lot were also delivered back to Barnes Engineering for some additional temperature and electrical tests. Barnes subjected them to a temperature of 62°C for 800 additional hours. These four devices withstood this additional test (total of 1640 hours) without any evidence of a noise problem.

A careful review of the test techniques and test circuitry at both Barnes and Ithaco showed that both sites apparently provided adequate protection for the test bolometers against voltage spikes and other circuit faults. Because of strict budgetary constraints, no further effort was made nor is contemplated to explore the erratic behavior of unsealed bolometers at Ithaco, especially since all space-flight bolometers are epoxy-sealed. Therefore, this bolometer study was terminated.

CONCLUSIONS AND RECOMMENDATIONS

The crystallinity problem of pure selenium glass films found in old bolometers was corrected. The new glass film deposition technique proved to be an operable procedure and was readily

implemented in the existing deposition process at Barnes. This method has now been adapted by Barnes as their new standard Se-As glass film evaporation procedure.

The results of this study and the one by M. K. El-Mously[3] suggest that the amount of As in the Se-As vapor deposited mixture can be varied anywhere from 5 to 18 At% and still inhibit the crystallization process in amorphous Se-As films. Other ratios of Se to As may be equally as effective in inhibiting Se crystallization, but were not studied.

Contradictory noise test results were found between the Barnes and the Ithaco test laboratories on unsealed bolometers. No such contradiction existed for sealed bolometers, as used in this limited study.

For long-term storage of epoxy-sealed devices, it is advisable to store them in a dry N_2 atmosphere to preclude possible atmospheric reactions with moisture and oxygen.

REFERENCES

1. Ithaco Summary Report, R. Kiefer, V. Selby, "Bolometer Failure Study," 10 April 1978.

2. Lockheed Interdepartmental Communication. G. Nothstein to S. S. Sagaw, "Trip Report-Bolometer Failure Investigation – Barnes Engineering Company," 10 June 1970.

3. M. K. El-Mously, "Effect of Heat Treatment on the Electrical Properties of Selenium," Indian Journal of Technology, Vol. II, April 1973, pp 167-169.

4. W. H. Rolls, "Selenium Immersed Thermistor Bolometer Study," Final Technical Report, June 1979.

5. R. Kiefer, "Final Report, Tarpley Bolometer Burn-in at 50°C, Contract: GSFC NAS5-20860," February 27, 1980.

ACKNOWLEDGMENTS

The authors greatly appreciate and acknowledge the significant contributions made to this study by the following individuals: P. Cudmore, S. Kant, A. Babecki, and W. Viehmann for technical guidance and in failure analysis consultations; to J. Jellison and M. Barthelmy for Metallographic preparations and studies; to R. Marriott for extensive SEM analyses and for computer programming; to J. Colony, for IR spectrographic analyses, to O. Faut for assistance with chemical analyses; and finally to W. Rolls of Barnes and R. Kiefer of Ithaco for their contractual support.

Table 1

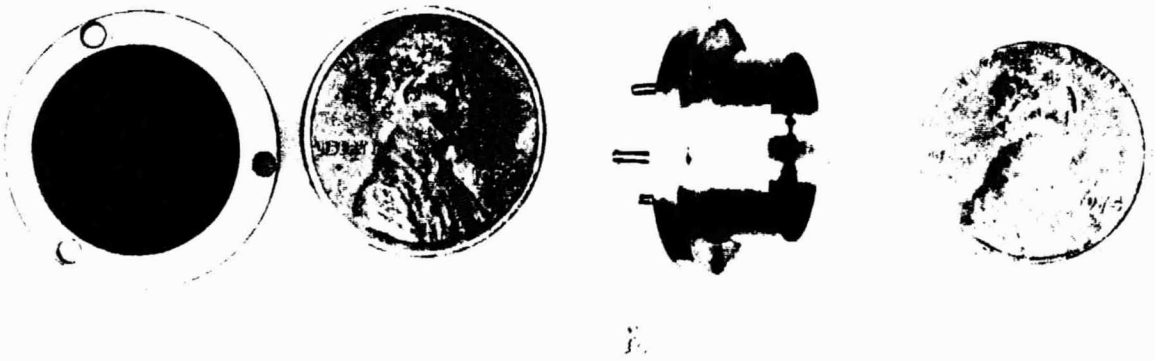
Sample No.	Initial Powder Mixture Se-As, At%	EDAX Analysis[1] Se-As, At%		γ^2	n^3
2942	87.43-12.57	Pellet	86.30-13.70	0.98	5
2942		Glass Film	84.85-15.15	1.15	5
2945	87.43-12.57	Pellet	84.66-15.34	1.01	5
2945		Glass Film	81.57-18.43	0.88	5
2962	91.89-8.11	Pellet	90.38-9.62	0.80	5
2962		Glass Film	87.06-12.94	0.83	5

Notes:

1 Pellet is a proportioned mixture of Se-As that has been melted into a conglomerate, quenched, then broken into small fragments and stored for future vapor deposition. Glass film is the vapor deposited Se-As insulating film layer obtained from the pellet.

2 γ is the standard deviation from the At% values.

3 n is the number of times each test sample was analyzed.



A. TOP VIEW SHOWING FLAT Ge LENS

B. SIDE VIEW SHOWING MODULAR PLUG-IN BASE

Figure 1. Sealed Experimental Bolometer Assembly
Comparable in Diameter to a Penny

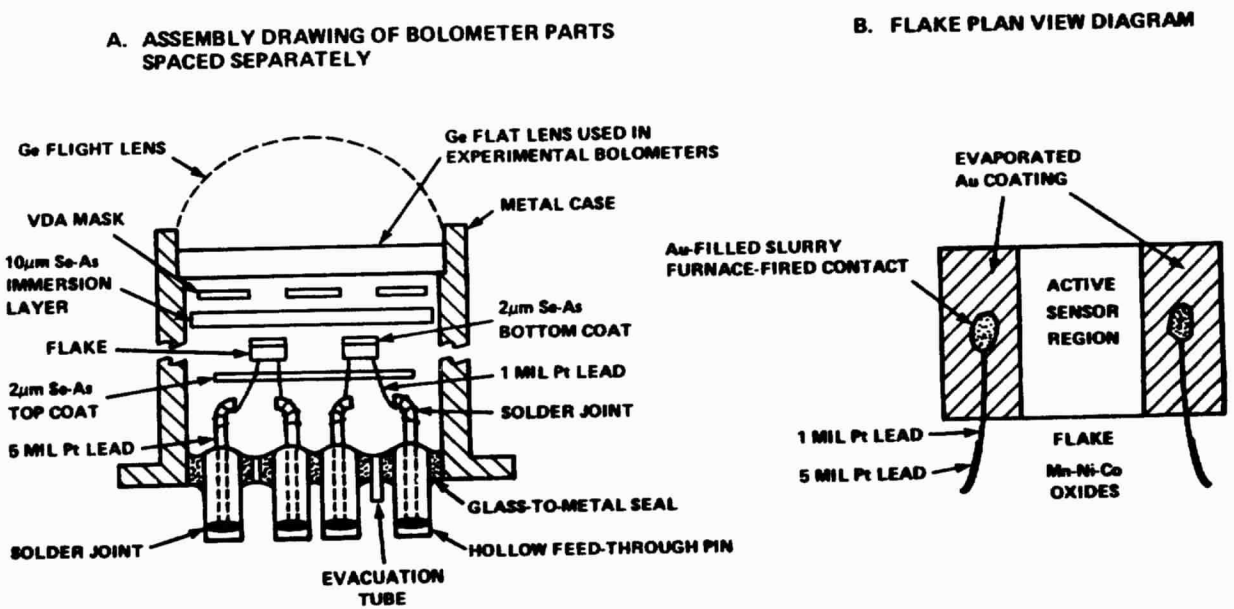


Figure 2. Basic Bolometer Parts

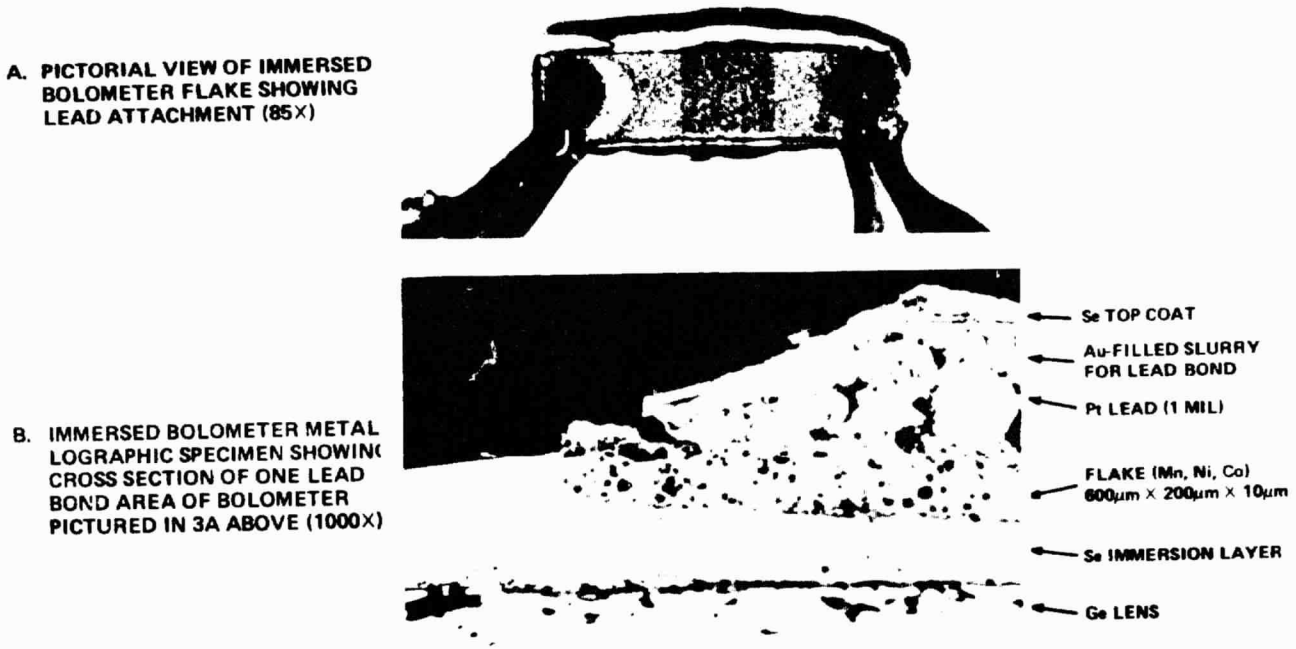


Figure 3. Pictorial View of Immersed Bolometer

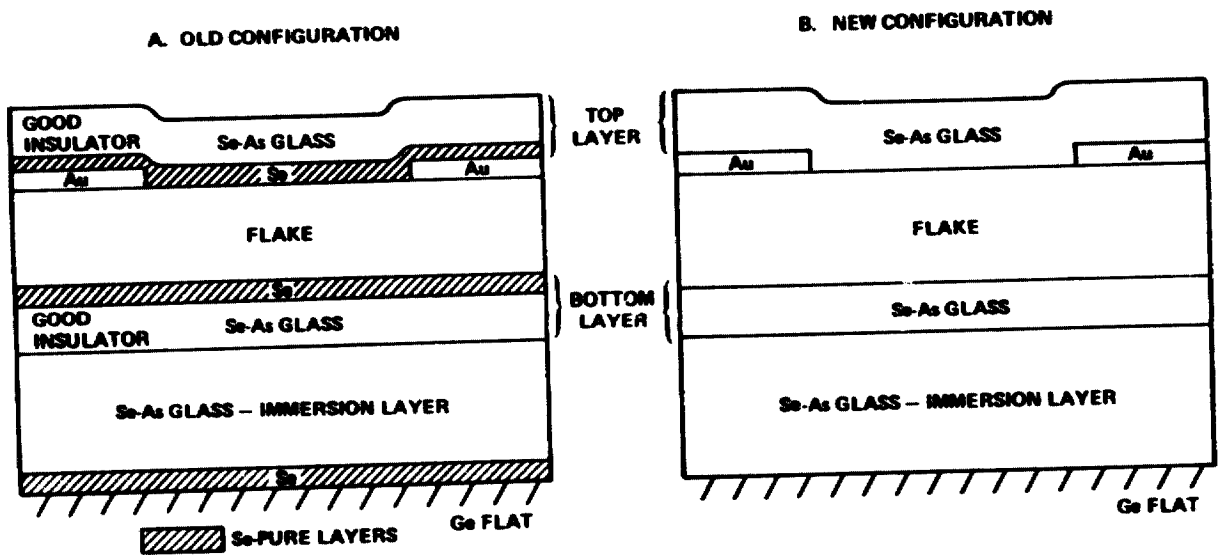


Figure 4. Old and New Flake Configuration

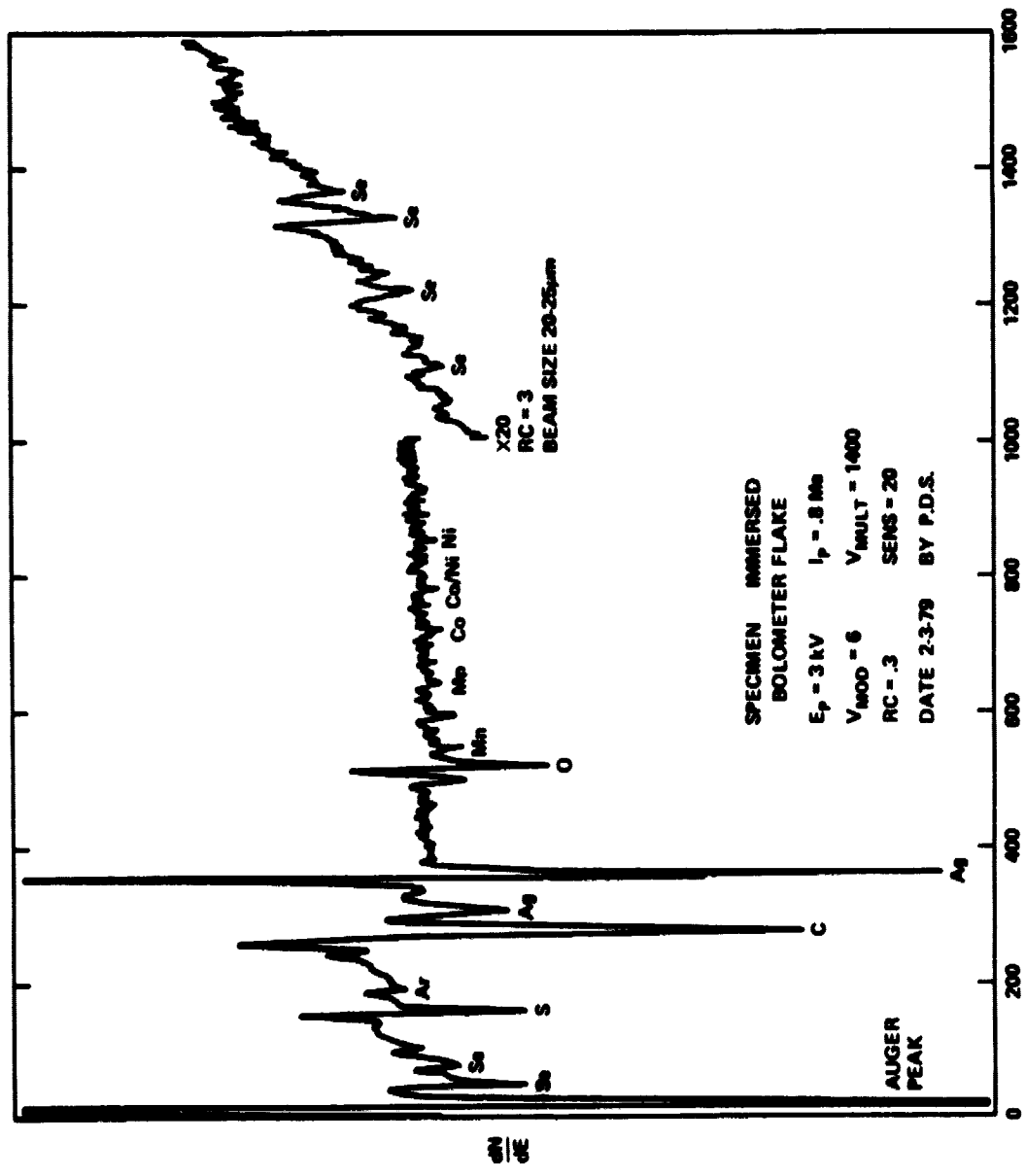


Figure 5. Se-Rich Film Layer on Immersed Flake From Old Evaporation Technique

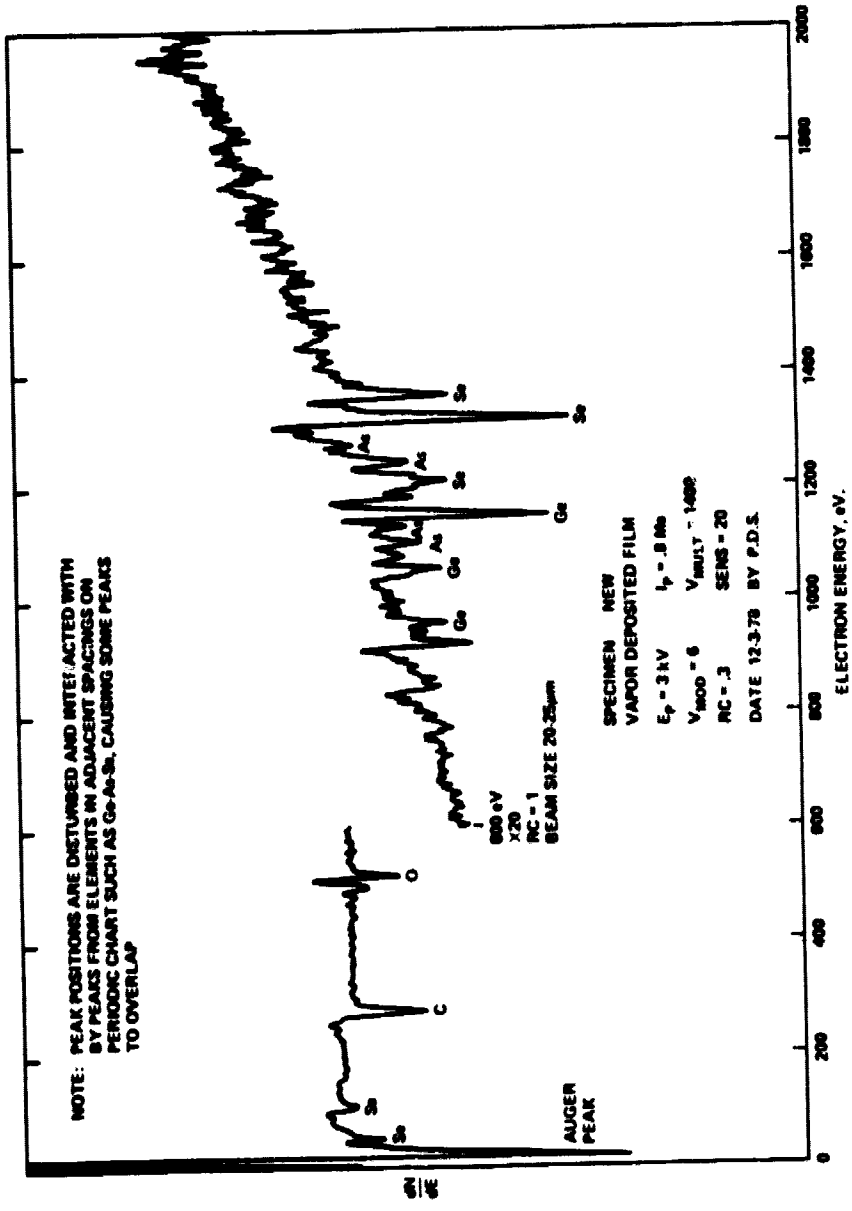


Figure 6. Composite Se-As Film Layer at Ge Disc Surface From New Evaporation Technique

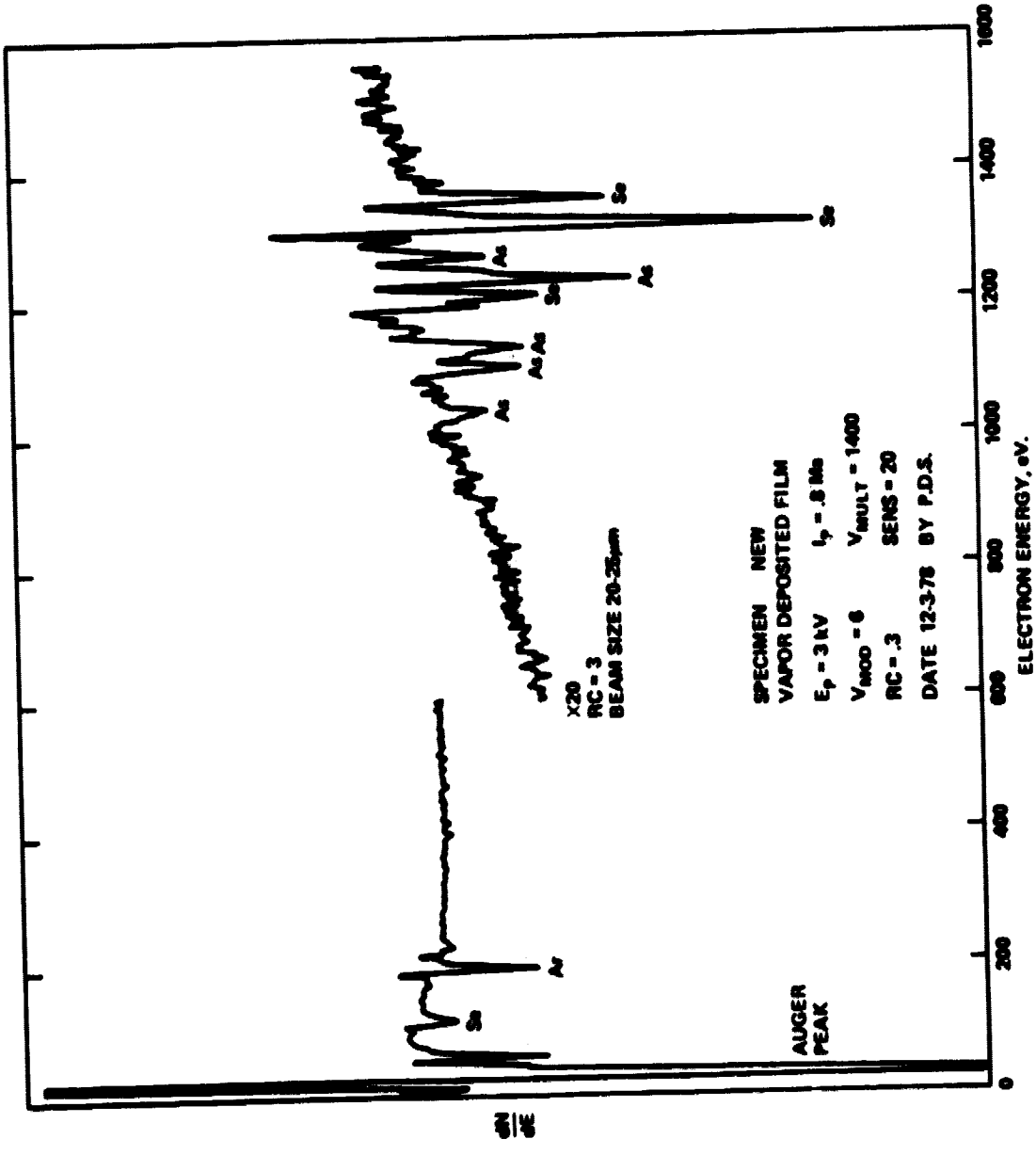


Figure 7. Composite Se-As Film Layer From New Evaporation Technique

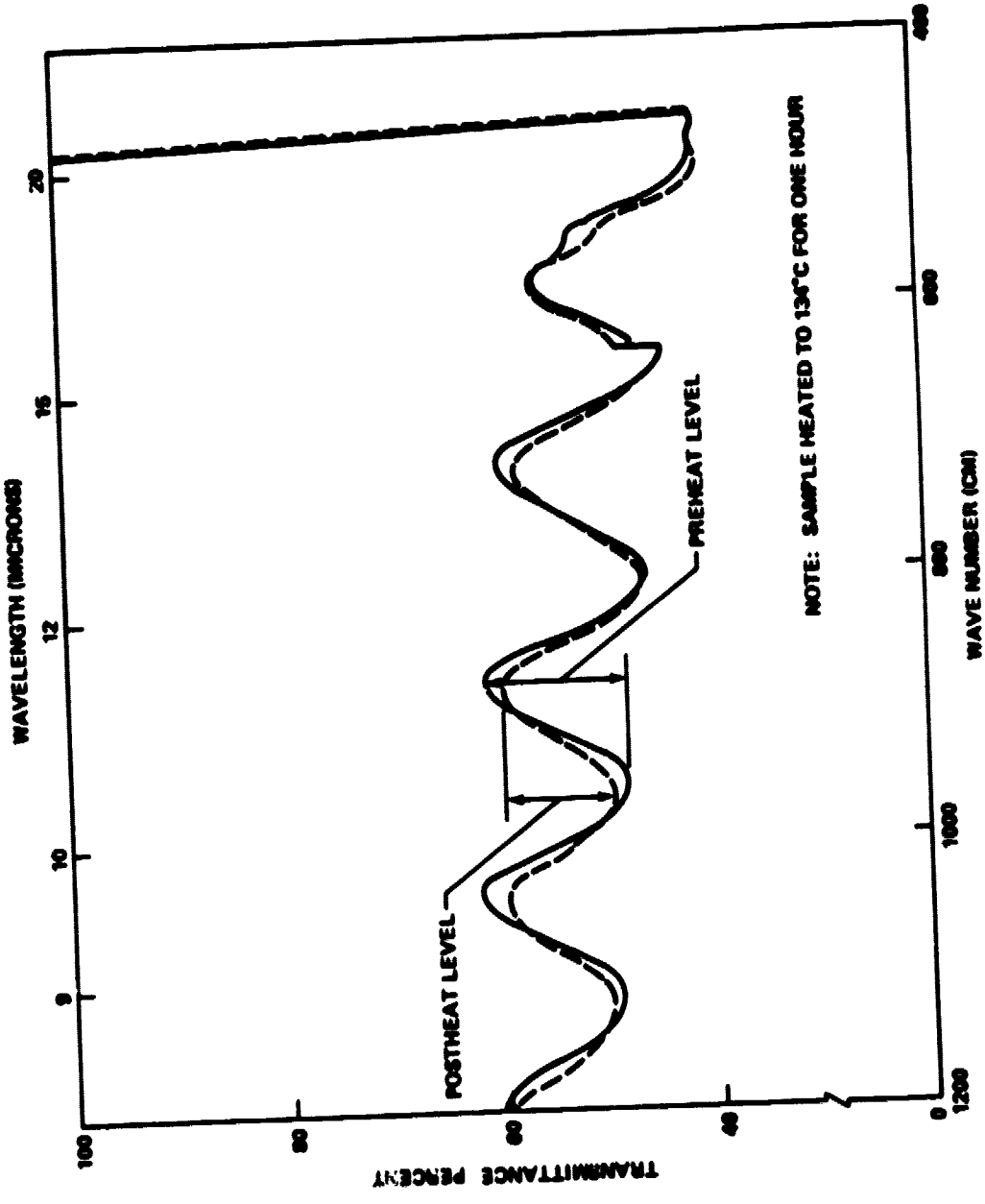


Figure 8. IR Divergence Shown in Old Process Evaporated Film Due to Heat

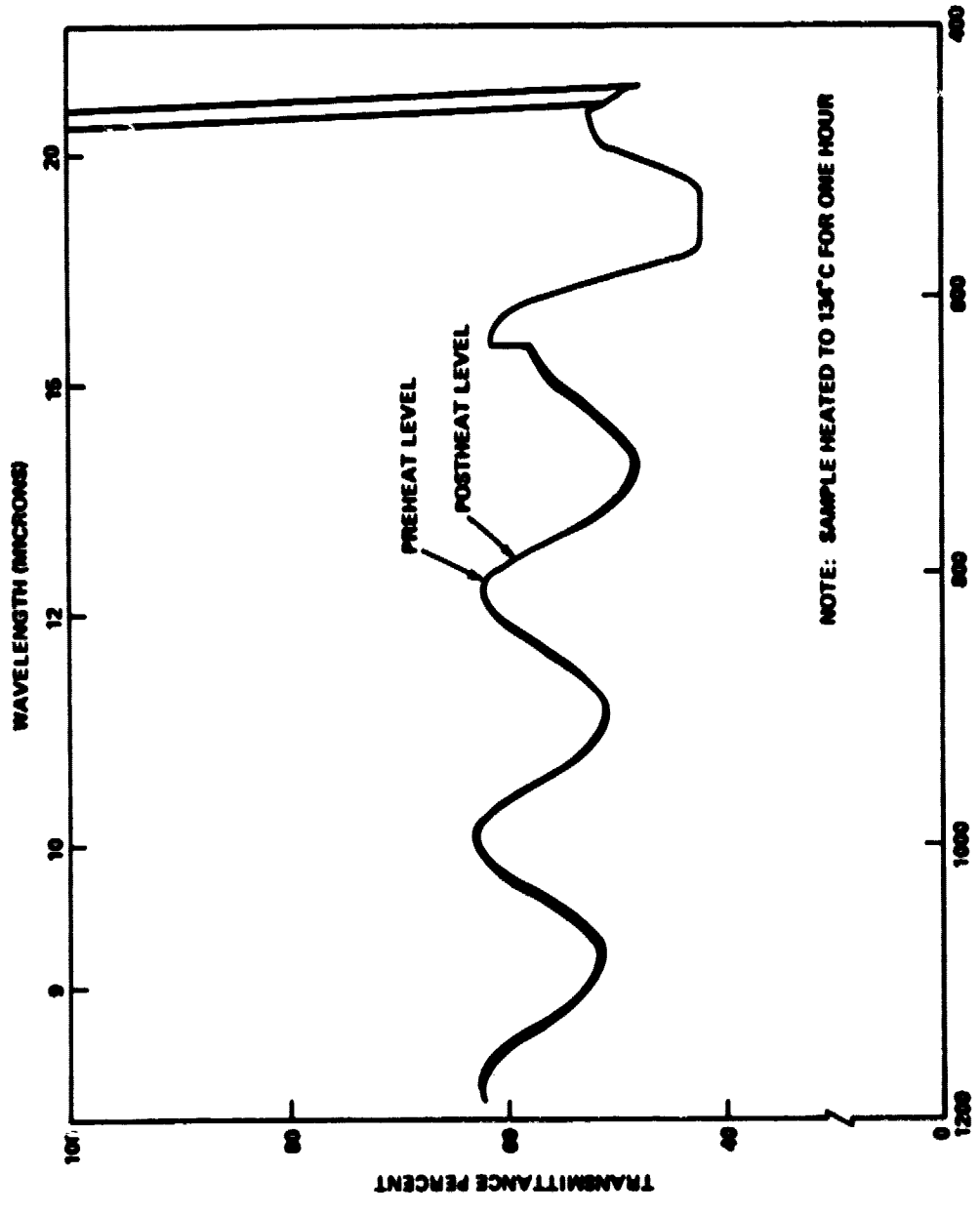


Figure 9. IR Response Unchanged, After Heating New Process Evaporated Film

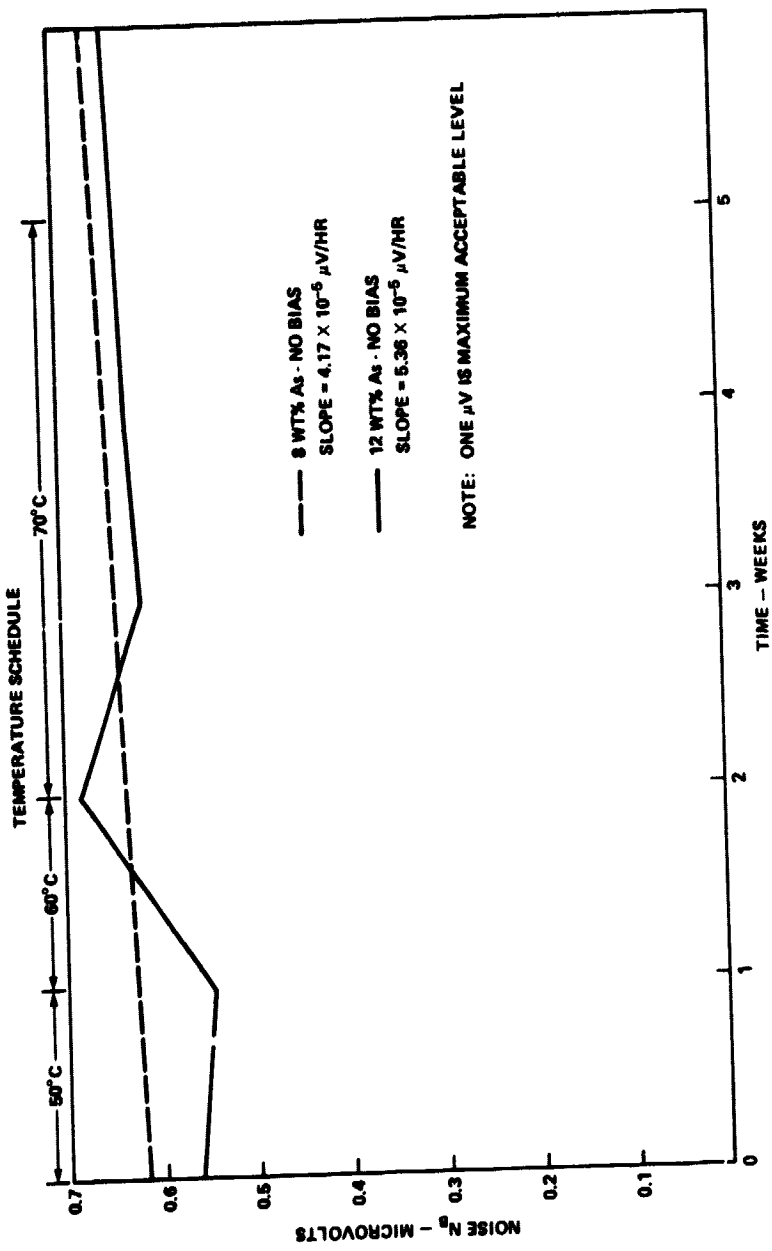


Figure 10. Noise Versus Time/Temperature on Unbiased Bolometers

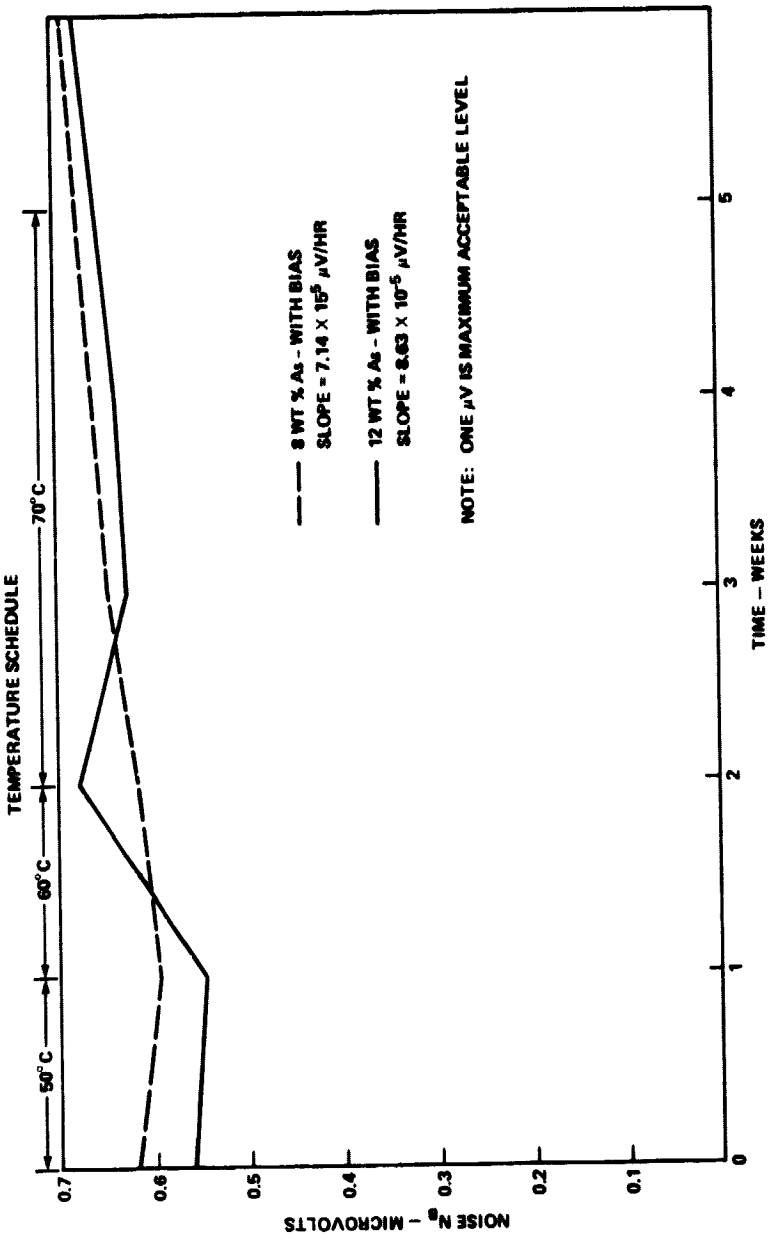


Figure 11. Noise Versus Time/Temperature on Biased Bolometers

BIBLIOGRAPHIC DATA SHEET

1. Report No. TM 82001	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Investigation of Electrical Noise in Selenium-Immersed Thermistor Bolometers		5. Report Date August 1980 6. Performing Organization Code 313
7. Author(s) John L. Tarpley and Pedro D. Sarmiento		8. Performing Organization Report No.
9. Performing Organization Name and Address Materials Control and Applications Branch		10. Work Unit No. 11. Contract or Grant No. 13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address Goddard Space Flight Center Greenbelt, Maryland 20771		14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

The selenium-immersed, thermistor-bolometer, IR detector has a history marked by failure due to spurious and escalating electrical noise outburst as a function of time at elevated temperatures. These failures were observed during routine ground-based testing in a space-simulated environment. Spectrographic analysis of failed bolometers revealed selenium-pure zones in the insulating selenium-arsenic (Se-As) glass film which surrounds the active sintered Mn, Ni, Co oxide flake. The selenium-pure film was identified as a potentially serious failure mechanism. Therefore, significant changes were instituted in the manufacturing techniques and, along with more stringent process controls, these changes effectively eliminated the selenium-pure film and successfully produced 22 study bolometers.

Independent bolometer testing of electrical stability at two different test laboratories gave conflicting test results on unsealed units. Barnes laboratory tests revealed no anomalous noise fluctuations or excursions on 22 units whereas Ithaco laboratory tests showed a very rapid noise buildup on 11 units tested by them. The reason for the conflict was not determined. However, bolometers that were deliberately sealed as required for space flight use and then tested up to 50°C for 2000 hours continuously performed well within electrical noise specifications at Ithaco.

17. Key Words (Selected by Author(s))	18. Distribution Statement
Selenium-Immersed Bolometers Noise Investigation	

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*

*For sale by the National Technical Information Service, Springfield, Virginia 22151.

GSFC 25-44 (10/77)